Presidential Green Chemistry Challenge

2005 Award Recipients

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Note: The summaries provided in this document were obtained from the entries received for the 2005 Presidential Green Chemistry Challenge Awards. EPA edited the descriptions for space, stylistic consistency, and clarity, but they were not written or officially endorsed by EPA. The summaries are intended only to highlight a fraction of the information contained in the nominated projects. These summaries were not used in the judging process; judging was conducted on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.

Academic Category

Professor Robin D. Rogers, The University of Alabama

A Platform Strategy Using Ionic Liquids to Dissolve and Process Cellulose for Advanced New Materials

Major chemical companies are currently making tremendous strides towards using renewable resources in biorefineries. In a typical biorefinery, the complexity of natural polymers, such as cellulose, is first broken down into simple building blocks (e.g., ethanol, lactic acid), then built up into complex polymers. If one could use the biocomplexity of natural polymers to form new materials directly, however, one could eliminate many destructive and constructive synthetic steps. Professor Rogers and his group have successfully demonstrated a platform strategy to efficiently exploit the biocomplexity afforded by one of Nature's renewable polymers, cellulose, potentially reducing society's dependence on nonrenewable petroleum-based feedstocks for synthetic polymers. No one had exploited the full potential of cellulose previously, due in part to the shift towards petroleum-based polymers since the 1940s, difficulty in modifying the cellulose polymer properties, and the limited number of common solvents for cellulose.

Professor Rogers's technology combines two major principles of green chemistry: developing environmentally preferable solvents and using biorenewable feedstocks to form advanced materials. Professor Rogers has found that cellulose from virtually any source (fibrous, amorphous, pulp, cotton, bacterial, filter paper, etc.) can be dissolved readily and rapidly, without derivatization, in a low-melting ionic liquid (IL), 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) by gentle heating (especially with microwaves). IL-dissolved cellulose can easily be reconstituted in water in controlled architectures (fibers, membranes, beads, flocs, etc.) using conventional extrusion spinning or forming techniques. By incorporating functional additives into the solution before reconstitution, Professor Rogers can prepare blended or composite materials. The incorporated functional additives can be either dissolved (e.g., dyes, complexants, other polymers) or dispersed (e.g., nanoparticles, clays, enzymes) in the IL before or after dissolution of the cellulose. With this simple, noncovalent approach, Professor Rogers can readily prepare encapsulated cellulose composites of tunable architecture, functionality, and rheology. The IL can be recycled by a novel salting-out step or by common cation exchange, both of which save energy compared to recycling by distillation.

Professor Rogers's current work is aimed at improved, more efficient, and economical syntheses of [C_4mim]Cl, studies of the IL toxicology, engineering process development, and commercialization.

Professor Rogers and his group are currently doing market research and business planning leading to the commercialization of targeted materials, either through joint development agreements with existing chemical companies or through the creation of small businesses. Green chemistry principles will guide the development work and product selection. For example, targeting polypropylene- and polyethylene-derived thermoplastic materials for the automotive industry could result in materials with lower cost, greater flexibility, lower weight, lower abrasion, lower toxicity, and improved biodegradability, as well as significant reductions in the use of petroleum-derived plastics.

Professor Rogers's work combines a fundamental knowledge of ILs as solvents with a novel technology for dissolving and reconstituting cellulose and similar polymers. Using green chemistry principles to guide process development and commercialization, he envisions that his platform strategy can lead to a variety of commercially viable advanced materials that will obviate or reduce the use of synthetic polymers.

Small Business Category

Metabolix, Inc.

Producing Nature's Plastics Using Biotechnology

Metabolix is commercializing polyhydroxyalkanoates (PHAs), a broadly useful family of natural, environmentally friendly, high-performing, biobased plastics. PHAs are based on a biocatalytic process that uses renewable feedstocks, such as cornstarch, cane sugar, cellulose hydrolysate, and vegetable oils. PHAs can provide a sustainable alternative to petrochemical plastics in a wide variety of applications.

Metabolix uses biotechnology to introduce entire enzyme-catalyzed reaction pathways into microbes, which then produce PHAs, in effect creating living biocatalysts. The performance of these engineered microbes has been fully validated in commercial equipment, demonstrating reliable production of a wide range of PHA copolymers at high yield and reproducibility. A highly efficient commercial process to recover PHAs has also been developed and demonstrated. The routine expression of exogenous, chromosomally integrated genes coding for the enzymes used in a non-native metabolic pathway is a *tour de force* in the application of biotechnology. These accomplishments have led Metabolix to form an alliance with Archer Daniels Midland Company, announced in November 2004, to produce PHAs commercially, starting with a 50,000 ton per year plant to be sited in the U.S. Midwest.

These new natural PHA plastics are highly versatile, have a broad range of physical properties, and are practical alternatives to synthetic petrochemical plastics. PHAs range from rigid to highly elastic, have very good barrier properties, and are resistant to hot water and greases. Metabolix has developed PHA formulations suitable for processing on existing equipment and demonstrated them in key end-use applications such as injection molding, thermoforming, blown film, and extrusion melt casting including film, sheet, and paper coating.

Metabolix's PHA natural plastics will bring a range of environmental benefits, including reduced reliance on fossil carbon and reduced greenhouse gas emissions. PHAs are now made from renewable raw materials, such as sugar and vegetable oils. In the future, they will be produced directly in plants. In addition, PHAs will reduce the burden of plastic waste on solid waste systems, municipal waste treatment systems, and marine and wetlands ecosystems: they will biodegrade to harmless products in a wide variety of both aerobic and anaerobic environments, including soil, river and ocean water, septic systems, anaerobic digesters, and compost.

Metabolix's PHA technology is the first commercialization of plastics based on renewable resources that employs living biocatalysts in microbial fermentation to convert renewable raw materials all the way to the finished copolymer product. PHAs are also the first family of plastics that combine broadly useful properties with biodegradability in a wide range of environments, including marine and wetlands ecosystems. Replacement of petrochemical plastics with PHAs will also have significant economic benefits. Producing 25 million tons of PHA natural plastics to replace about half of the petrochemical plastics currently used in the U.S. would reduce oil imports by over 200 to 230 million barrels per year, improving the U.S. trade balance by $6 to 9 billion a year, assuming oil at $30 to $40 per barrel.

Alternative Synthetic Pathways Category

Archer Daniels Midland Company
Novozymes

NovaLipid™: Low *Trans* Fats and Oils Produced by Enzymatic Interesterification of Vegetable Oils Using Lipozyme®

Two major challenges facing the food and ingredient industry are providing health-conscious products to the public and developing environmentally responsible production technology. Archer Daniels Midland Company (ADM) and Novozymes are commercializing enzymatic interesterification, a technology that not only has a tremendous positive impact on public health by reducing *trans* fatty acids in the American diet, but also offers great environmental benefits by eliminating the waste streams generated by the chemical interesterification process.

Triglycerides consist of one glycerol plus three fatty acids. Triglycerides that contain mostly unsaturated fatty acids are liquid at room temperature. Manufacturers partially hydrogenate these fatty acids to make them solids at room temperature. *Trans* fatty acids form during the hydrogenation process; they are found at high concentrations in a wide variety of processed foods. Unfortunately, consumption of *trans* fatty acids is also a strong risk factor for heart disease. To reduce *trans* fats in the American diet as much as possible, the FDA is now requiring labeling of *trans* fats on all nutritional fact panels by January 1, 2006. In response, the U.S. food and ingredient industry has been investigating methods to reduce *trans* fats in food.

Of the available strategies, interesterification is the most effective way to decrease the *trans* fat content in foods without sacrificing the functionality of partially hydrogenated vegetable oils. During interesterification, triglycerides containing saturated fatty acids exchange one or two of their fatty acids with triglycerides containing unsaturated fatty acids, resulting in triglycerides that do not contain any *trans* fatty acids. Enzymatic interesterification processes have many benefits over chemical methods, but the high cost of the enzymatic process and poor enzyme stability had prevented its adoption in the bulk fat industry.

Extensive research and development work by both Novozymes and ADM has led to the commercialization of an enzymatic interesterification process. Novozymes developed a cost- effective immobilized enzyme, and ADM developed a process to stabilize the immobilized enzyme enough for successful commercial production. The interesterified oil provides food companies with broad options for zero and reduced *trans* fat food products. Since the first commercial production in 2002, ADM has produced more than 15 million pounds of interesterified oils. ADM is currently expanding the enzyme process at two of its U.S. production facilities.

Enzymatic interesterification positively affects both environmental and human health. Environmental benefits include eliminating the use of several harsh chemicals, eliminating byproducts and waste streams (solid and water) and improving the use of edible oil resources. As one example, margarines and shortenings currently consume 10 billion pounds of hydrogenated soybean oil each year. Compared to partial hydrogenation, the ADM/Novozymes process has the potential to save 400 million pounds of soy bean oil, eliminate 20 million pounds of sodium methoxide, 116 million pounds of soaps, 50 million pounds of bleaching clay, and 60 million gallons of water each year. The enzymatic process also contributes to improved public health by replacing partially hydrogenated oils with interesterified oils that contain no *trans* fatty acids and have increased polyunsaturated fatty acids.

Alternative Synthetic Pathways Category

Merck & Co., Inc.

A Redesigned, Efficient Synthesis of Aprepitant, the Active Ingredient in Emend®: A New Therapy for Chemotherapy-Induced Emesis

Emend® is a new therapy for chemotherapy-induced nausea and vomiting, the most common side effects associated with chemotherapeutic treatment of cancer. Emend® has been clinically shown to reduce nausea and vomiting when used during and shortly after chemotherapy. Aprepitant is the active pharmaceutical ingredient in Emend®.

Aprepitant, which has two heterocyclic rings and three stereogenic centers, is a challenging synthetic target. Merck's first-generation commercial synthesis required six synthetic steps and was based on the discovery synthesis. The raw material and environmental costs of this route, however, along with operational safety issues compelled Merck to discover, develop, and implement a completely new route to aprepitant.

Merck's new route to aprepitant demonstrates several important green chemistry principles. This innovative and convergent synthesis assembles the complex target in three highly atom-economical steps using four fragments of comparable size and complexity. The first-generation synthesis required stoichiometric amounts of an expensive, complex chiral acid as a reagent to set the absolute stereochemistry of aprepitant. In contrast, the new synthesis incorporates a chiral alcohol as a feedstock; this alcohol is itself synthesized in a catalytic asymmetric reaction. Merck uses the stereochemistry of this alcohol feedstock in a practical crystallization-induced asymmetric transformation to set the remaining stereogenic centers of the molecule during two subsequent transformations. The new process nearly doubles the yield of the first-generation synthesis. Much of the chemistry developed for the new route is novel and has wider applications. In particular, the use of a stereogenic center that is an integral part of the final target molecule to set new stereocenters with high selectivity is applicable to the large-scale synthesis of other chiral molecules, especially drug substances.

Implementing the new route has drastically improved the environmental impact of aprepitant production. Merck's new route eliminates all of the operational hazards associated with the first-generation synthesis, including those of sodium cyanide, dimethyl titanocene, and gaseous ammonia. The shorter synthesis and milder reaction conditions have also reduced the energy requirements significantly. Most important, the new synthesis requires only 20% of the raw materials and water used by the original one. By adopting this new route, Merck has eliminated approximately 340,000 liters of waste per 1,000 kg of aprepitant that it produces.

The alternative synthetic pathway for the synthesis of aprepitant as discovered and implemented by Merck is an excellent example of minimizing environmental impact while greatly reducing production costs by employing the principles of green chemistry. Merck implemented the new synthesis during its first year of production of Emend®; as a result, Merck will realize the benefits of this route for virtually the entire lifetime of this product. The choice to implement the new route at the outset of production has led to a huge reduction in the cost to produce aprepitant, demonstrating quite clearly that green chemistry solutions can be aligned with cost-effective ones.

Alternative Solvents/ Reaction Conditions Category

BASF Corporation

A UV-Curable, One-Component, Low-VOC Refinish Primer: Driving Eco-Efficiency Improvements

The market for automotive refinish coatings in North America exceeds $2 billion for both collision repairs and commercial vehicle applications. Over 50,000 body shops in North America use these products. For more than a decade, automotive refinishers and coating manufacturers have dealt with increasing regulation of emissions of volatile organic compounds (VOCs). At first, coating manufacturers were able to meet VOC maximums with high-performance products such as two-component reactive urethanes, which require solvents as carriers for their high-molecular-weight resins. As thresholds for VOCs became lower, however, manufacturers had to reformulate their reactive coatings, and the resulting reformulations were slow to set a film. Waterborne coatings are also available, but their utility has been limited by the time it takes the water to evaporate. Continuing market pressures demanded faster film setting without compromising either quality or emissions.

Through intense research and development, BASF has invented a new urethane acrylate oligomer primer system. The resin cross-links with monomer (added to reduce viscosity) into a film when the acrylate double bonds are broken by radical propagation. The oligomers and monomers react into the film's cross-linked structure, improving adhesion, water resistance, solvent resistance, hardness, flexibility, and cure speed. The primer cures in minutes by visible or near-ultraviolet (UV) light from inexpensive UV-A lamps or even sunlight. BASF's UV-cured primer eliminates the need for bake ovens that cure the current primers, greatly reducing energy consumption. BASF's primer performs better than the current conventional urethane technologies: it cures ten times faster, requires fewer preparation steps, has a lower application rate, is more durable, controls corrosion better, and has an unlimited shelf life. BASF is currently offering its UV-cured primers in its R-M® line as Flash Fill™ VP126 and in its Glasurit® line as 151-70.

BASF's primer contains only 1.7 pounds of VOCs per gallon, in contrast to 3.5 to 4.8 pounds of VOCs per gallon of conventional primers, a reduction of over 50%. The primer meets even the stringent requirements of South Coast California, whereas its superior properties ensure its acceptance throughout the U.S. market. The one-component nature of the product reduces hazardous waste and cleaning of equipment, which typically requires solvents. Applications in repair facilities over the past year have shown that only one-third as much primer is needed and that waste is reduced from 20% to nearly zero. The BASF acrylate-based technology requires less complex, less costly personal protective equipment (PPE) than the traditional isocyanate-based coatings; this, in turn, increases the probability that small body shops will purchase and use the PPE, increasing worker safety.

This eco-efficient product is the first step in an automobile refinishing coating system for which BASF plans to include the globally accepted waterborne basecoat from BASF (sold under the Glasurit® brand as line 90). In the near future, this system can be finished with the application of a one-component, UV-A-curable clearcoat. The system will deliver quality, energy efficiency, economy, and speed for the small businessman operating a local body shop, while respecting the health and safety of the workers in this establishment and the environment in which these products are manufactured and used. To fully support these claims, BASF has conducted an eco-efficiency study with an independent evaluation.

Designing Safer Chemicals Category

Archer Daniels Midland Company

Archer RC™: A Nonvolatile, Reactive Coalescent for the Reduction of VOCs in Latex Paints

Since the 1980s, waterborne latex coatings have found increasingly broad acceptance in architectural and industrial applications. Traditional latex coatings are based on small-particle emulsions of a synthetic resin, such as acrylate- and styrene-based polymers. They require substantial quantities of a coalescent to facilitate the formation of a coating film as water evaporates after the coating is applied. The coalescent softens (plasticizes) the latex particles, allowing them to flow together to form a continuous film with optimal performance properties. After film formation, traditional coalescents slowly diffuse out of the film into the atmosphere. The glass transition temperature of the latex polymer increases as the coalescent molecules evaporate, and the film hardens. Alcohol esters and ether alcohols, such as ethylene glycol monobutyl ether (EGBE) and Texanol® (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), are commonly used as coalescents. They are also volatile organic compounds (VOCs). Both environmental concerns and economics continue to drive the trend to reduce the VOCs in coating formulations. Inventing new latex polymers that do not require a coalescent is another option, but these polymers often produce soft films and are expensive to synthesize, test, and commercialize. Without a coalescent, the latex coating may crack and may not adhere to the substrate surface when dry at ambient temperatures.

Archer RC™ provides the same function as traditional coalescing agents, but eliminates the unwanted VOC emissions. Instead of evaporating into the air, the unsaturated fatty acid component of Archer RC™ oxidizes and even cross-links into the coating. Archer RC™ is produced by interesterifying vegetable oil fatty acid esters with propylene glycol to make the propylene glycol monoesters of the fatty acids. Corn and sunflower oils are preferred feedstocks for Archer RC™ because they have a high level of unsaturated fatty acids and tend to resist the yellowing associated with linolenic acid, found at higher levels in soybean and linseed oils. Because Archer RC™ remains in the coating after film formation, it adds to the overall solids of a latex paint, providing an economic advantage over volatile coalescents.

The largest commercial category for latex paint, the architectural market, was 618.4 million gallons in the U.S. in 2001. Typically, coalescing solvents constitute 2 to 3% of the finished paint by volume; this corresponds to an estimated 120 million pounds of coalescing solvents in the U.S. and perhaps three times that amount globally. Currently, nearly all of these solvents are lost into the atmosphere each year.

Archer Daniels Midland Company has developed and tested a number of paint formulations using Archer RC™ in place of conventional coalescing solvents. In these tests, Archer RC™ performed as well as commercial coalescents such as Texanol®. Archer RC™ often had other advantages as well, such as lower odor, increased scrub resistance, and better opacity. Paint companies and other raw material suppliers have demonstrated success formulating paints with Archer RC™ and their existing commercial polymers. Archer RC™ has been in commercial use since March 2004.